PB-238 092

GUIDELINES FOR DETERMINING PERFORMANCE CHARACTERISTICS OF AUTOMATED METHODS FOR MEASURING NITROGEN DIOXIDE AND HYDROCARBONS CORRECTED FOR METHANE IN AMBIENT AIR

National Environmental Research Center
Research Triangle Park, North Carolina

November 1974

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

Research reports of the Office of Research and Development, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL MONITORING series. This series describes research conducted to develop new or improved methods and instrumentation for the identification and quantification of environmental pollutants at the lowest conceivably significant concentrations. It also includes studies to determine the ambient concentrations of pollutants in the environment and/or the variance of pollutants as a function of time or meteorological factors.

Copies of this report are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - as supplies permit - from the Air Pollution Technical Information Center, Environmental Protection Agency, Research Triangle Park, North Carolina 27711; or, for a fee, from the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	PB 238 092
EPA-650/4-74-018		

4. TITLE AND SUBTITLE	5. REPORT DATE
Guidelines for Determining Performance Characteristics of Automated Methods for Measuring Nitrogen Dioxide and Hydrocarbons Corrected for Methane in Ambient Air	November 1974
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Quality Assurance and Environmental Monitoring Lab. National Environmental Research Center Research Triangle Park, North Carolina 27711	10. PROGRAM ELEMENT NO. 1HA327
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Recommended performance specification and test procedures are given for range, noise, lower detectable limit, interference equivalent, zero drift, span drift, lag time, rise time, fall time, and precision for automated methods for measuring nitrogen dioxide and hydrocarbons corrected for methane.

These specifications and test procedures are intended for use as guidelines to assist instrument manufacturers and instrument users to determine performance characteristics for continuous air monitoring analyzers.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Performance specification Nitrogen dioxide Hydrocarbons Air monitoring analyzers		

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Unlimited	Unclassified	47
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

EPA-650/4-74-018

GUIDELINES FOR DETERMINING PERFORMANCE CHARACTERISTICS OF AUTOMATED METHODS FOR MEASURING NITROGEN DIOXIDE AND HYDROCARBONS CORRECTED FOR METHANE IN AMBIENT AIR

by

Quality Assurance and Environmental
Monitoring Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina

Program Element No. 1HA327

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

November 1974

1a

This report has been reviewed by the Office of Research and Monitoring, Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Publication No. EPA-650/4-74-018

CONTENTS

	Page
LIST OF TABLES	iv
LIST OF FIGURES	iv
ABSTRACT	v
INTRODUCTION	1
1. Proposed Regulations for Determining Equivalency	1
2. Nitrogen Dioxide	2
3. Hydrocarbons Corrected for Methane	3
4. Guidelines	4
TEST PROCEDURES FOR MEASURING PERFORMANCE CHARACTERISTICS	7
1. General Provisions	7
2. Test Conditions	10
3. Generation of Test Atmospheres	12
4. Test Procedures	15
a. Range	15
b. Noise	15
c. Lower Detectable Limit	18
d. Interference Equivalent	20
e. Zero Drift, Span Drift, Lag Time, Rise Time, Fall Time, and Precision	24

LIST OF TABLES

		Page
Table 1.	Performance Specifications.	9
Table 2.	Test Atmospheres.	13
Table 3.	Interferent Test Concentration.	21
Table 4.	Line Voltage and Room Temperature Test Conditions . .	27
Table 5.	Symbols and Abbreviations	40

LIST OF FIGURES

		Page
Figure 1.	Form for Noise Data.	17
Figure 2.	Form for Data and Calculations for Lower Detectable Limit and Interference Equivalent	19
Figure 3.	Example of Typical Strip Chart Trace for the Test Procedure for Drift, Lag Time, Rise Time, Fall Time, and Precision	29
Figure 4.	Form for Recording Data for Drift and Precision. . .	31
Figure 5.	Form for Calculating for Zero Drift, Span Drift, and Precision.	35
Figure 6.	Form for Summary of Test Results	39

ABSTRACT

Recommended performance specification and test procedures are given for range, noise, lower detectable limit, interference equivalent, zero drift, span drift, lag time, rise time, fall time, and precision for automated methods for measuring nitrogen dioxide and hydrocarbons corrected for methane.

These specifications and test procedures are intended for use as guidelines to assist instrument manufacturers and instrument users to determine performance characteristics for continuous air monitoring analyzers.

INTRODUCTION

1. PROPOSED REGULATIONS FOR DETERMINING EQUIVALENCY

Pursuant to Sections 109 and 301 of the 1970 Amendments to the Clean Air Act (P.L. 91-604), the Administrator of the Environmental Protection Agency (EPA) promulgated on April 30, 1971, National Primary and Secondary Ambient Air Quality Standards for six air pollutants - sulfur dioxide, particulate matter, carbon monoxide, photochemical oxidants, hydrocarbons corrected for methane, and nitrogen dioxide.[1] This regulation included a "reference method" for each of the six pollutants and stated that the method, or an "equivalent method", must be used when conducting air quality measurements to demonstrate achievement of the standards. An equivalent method was defined as "any method of sampling and analyzing for an air pollutant which can be demonstrated to the Administrator's satisfaction to have a consistent relationship to the reference method."

The Administrator published on August 14, 1971, the Requirements for Preparation, Adoption, and Submittal of Implementation Plans, which amended the definition of an equivalent method to include the requirement that certain performance specifications be met.[2]

Regulations for the determination of equivalent and reference methods for measuring sulfur dioxide, carbon monoxide, and photochemical oxidants

---

[1] Code of Federal Regulations. Title 40 - Protection of Environment. Part 50 - National Primary and Secondary Ambient Air Quality Standards. Federal Register. 36(84): 8186, April 30, 1976.

[2] Code of Federal Regulations. Title 40 - Protection of Environment. Section 51.17 - Air Quality Surveillance. Federal Register. 36(158): 15492, August 14, 1971.

were proposed on October 12, 1973.[3] These regulations require that the burden of proving equivalence of a method rests with the requesting party, who must demonstrate that his method meets certain performance specifications and produces air quality data having a consistent relationship with data obtained by the reference method. Interested persons have submitted written comments on the proposed regulations, and, following consideration of the comments received, the regulations have been revised and are being promulgated as a new Part 53 entitled "Ambient Air Monitoring Equivalent and Reference Method Requirements" to Title 40 of the Code of Federal Regulations. Regulations for nitrogen dioxide and hydrocarbons corrected for methane were not included in the new Part 53 because of technical problems with the respective reference methods.

2. NITROGEN DIOXIDE

A reference method for nitrogen dioxide was set forth in Appendix F Part 50 of Title 40 of the Code of Federal Regulations. On June 14, 1972, however, EPA stated that the method was being re-evaluated. Results of laboratory testing and air quality measurements made over a period of several months at a large number of locations indicated several deficiencies.[4] On June 8, 1973, EPA announced its intention to amend Part 50 of Title 40 of the Code of Federal Regulations by withdrawing the original reference method for nitrogen dioxide.[5] In addition,

---

[3] Federal Register. 38(197): 28438, October 12, 1973.

[4] Federal Register. 37(115): 11826, June 14, 1972.

[5] Federal Register. 38(110): 11574, June 8, 1973.

EPA described three tentative methods being evaluated for possible use as reference methods. Upon promulgation of a new reference method for nitrogen dioxide, EPA will at the same time propose regulations for the determination of equivalent or reference methods for nitrogen dioxide.

3. HYDROCARBONS CORRECTED FOR METHANE

Section 51.14 of Title 40 of the Code of Federal Regulations[6] states that "it may be assumed that the degree of total hydrocarbon emission reduction necessary for the attainment and maintenance of national standard for photochemical oxidants will also be adequate for the attainment of the national standards for hydrocarbons." EPA, therefore, does not require the states to monitor hydrocarbons to determine compliance with national ambient air standards. The reference method for measuring hydrocarbons corrected for methane is a gas chromatographic technique that measures total hydrocarbons, methane, and carbon monoxide. Present commercially available instruments using this technique are expensive, complex, and demand considerable operator skill. They are marginal in their capability to measure hydrocarbons corrected for methane on a routine unattended basis at or below levels required by the national ambient air standard. Thus, because the states are not required to monitor hydrocarbons and because there are problems with the measurement methodology, EPA has not included hydrocarbons corrected for methane in the proposed equivalency determination regulations.

---

[6]Code of Federal Regulations. Title 40 - Protection of Environment. Section 51.14 Control Strategy. Federal Register. 36 (158): 15491, August 14, 1971.

4. GUIDELINES

Although EPA has not as yet proposed regulations for the determination of equivalent and reference methods for nitrogen dioxide and hydrocarbons corrected for methane, it has developed test procedures for measuring performance characteristics as well as recommended performance specifications for automated measurement methods for these pollutants. These test procedures and performance specifications are provided in this document and are intended as guidelines to help instrument manufacturers design, build, test, and describe the operating characteristics of their products. Instrument users will find the guidelines useful in developing procurement specifications and acceptance tests, as well as in enforcing warranties. In addition, the guidelines can assist in testing existing instruments to determine their adequacy for air quality measurements and in quality control auditing tests. Successful passage of the test procedures for measuring performance characteristics as described in these guidelines does not imply that the method tested can be used as an equivalent or reference method, however.

When a new reference method is established for nitrogen dioxide, EPA anticipates publishing regulations for the determination of equivalent and reference methods similar to those proposed for sulfur dioxide, carbon monoxide, and photochemical oxidants. The test procedures in this document are presented in a format similar to that of existing regulations in order to familiarize users of these guidelines with procedures likely to become regulations once a new reference method for nitrogen dioxide is designated. If regulations for equivalent methods become necessary for hydrocarbons corrected for methane, EPA

will likely produce corresponding regulations that will be similar to the guidelines presented here.

TEST PROCEDURES FOR MEASURING PERFORMANCE CHARACTERISTICS

1. GENERAL PROVISIONS

(a) The test procedures given herein may be used to test the performance of automated methods (i.e., analyzers) for measuring nitrogen dioxide and hydrocarbons corrected for methane against the minimum performance specifications given in Table 1 for each performance parameter. To satisfy the requirements of these guidelines, an analyzer must exhibit performance better than, or equal to, the specified value for each and all specifications listed.

(b) For each performance specification (except range), the test procedure is to be initially repeated seven (7) times, to yield seven (7) test results. Each result is to be compared with the corresponding specification in Table 1; a value higher or outside that specified constitutes a failure. These seven results for each parameter are then interpreted as follows:

(1) Zero (0) failures: analyzer passes the performance parameter.

(2) Three (3) or more failures: analyzer fails the performance parameter.

(3) One (1) or two (2) failures: repeat the test procedure for the parameter eight (8) additional times yielding a total of fifteen (15) test results. The combined total of

Preceding page blank

fifteen test results is interpreted as follows:

(i) One (1) or two (2) failures: analyzer passes the performance parameter.

(ii) Three (3) or more failures: analyzer fails the performance parameter.

(c) During conduct of these tests, the analyzer should be operated in the range specified in Table 1, or in any lower (more sensitive) range. The actual range used in the test should be clearly indicated. An analyzer may be operated in a higher (less sensitive) range if sufficient justification for such operation exists. For an analyzer capable of operation in two or more ranges (multiple range capability), appropriate test data should be obtained for each range available, and the analyzer must pass all performance specifications for each range to satisfy the requirements of this guideline.

(d) The tests for zero drift, span drift, lag time, fall time, rise time, and precision are combined into a single procedure which is conducted at various voltages and various ambient temperatures. The tests for noise, lower detectable limit, and interference equivalent are made at any temperature between 20°C and 30°C and at any normal line voltage between 105 and 125 volts, and are to be conducted such that not more than three (3) test results for each parameter are obtained per 24 hours.

(e) All analyzer response readings to be recorded should first be converted to concentration units according to the calibration curve.

(f) All recorder chart tracings, records, test data, and other documentation obtained from or pertinent to these tests should be identified, dated, and

Table 1. PERFORMANCE SPECIFICATIONS[a]

Performance parameter	Units[b]	NO_2	Hydrocarbons corrected for methane[c,d]
1. Range	ppm	0-0.5	0-5
2. Noise	ppm	0.005	0.05
3. Lower detectable limit	ppm	0.01	0.1
4. Interference equivalent:			
Each interferent	ppm	±0.02	±0.1
Total interferent	ppm	±0.04	±0.2
5. Zero drift, 12- and 24-hour	ppm	±0.02	±0.2
6. Span drift, 24-hour	percent	±5	±5
7. Lag time	minutes	20	10
8. Rise time, 95%	minutes	15	10
9. Fall time, 95%	minutes	15	10
10. Precision:			
20% of upper range limit	ppm	0.02	0.3
80% of upper range limit	ppm	0.03	0.3

[a]All performance specifications are subject to reevaluation at any time and may be subject to change if sufficient justification exists.

[b]To convert from ppm to $\mu g/m^3$ at 25°C and 760mm Hg, multiply by M.W./0.02447, where M.W. is the molecular weight of the gas.

[c]For analyzers that read only "total hydrocarbons" and "methane" separately, readings for hydrocarbons corrected for methane are derived as the total hydrocarbon reading minus the concurrent methane reading.

[d]Determine as methane or as methane equivalent: 1.0 ppm ethane = 2.0 ppm methane equivalent.

signed by the analyst performing the test. Suggested formats for reporting the test results and calculations are provided in Figures 1, 2, 4, 5, and 6.

2. TEST CONDITIONS

(a) Set-up and start-up of the analyzer shall be in strict accordance with the analyzer's operating instructions. (Allow adequate warm-up or stabilization time as indicated in the operating instructions before beginning the tests.) If the analyzer does not have an integral strip chart recorder, connect the analyzer output to a suitable strip chart recorder of the servo, null-balance type. This recorder should have a chart width of at least 25 centimeters, chart speeds up to 10 centimeters per hour, a response time of 1 second or less, a deadband of not more than 0.25 percent of full scale, and capability of either reading measurements at least 5 percent below zero or offsetting the zero by at least 5 percent.

(b) Calibration of the analyzer should be as indicated by the analyzer's operating instructions and as follows: If the chart recorder does not have below-zero capability, adjust either the analyzer's controls or the chart recorder to obtain a +5 percent offset-zero reading on the recorder chart to facilitate observing negative response or drift. If the analyzer is not capable of negative response, the analyzer (not recorder) must be operated with an offset zero. Construct a calibration curve by plotting recorder scale readings (ordinate) against pollutant concentrations (abscissa). A plot of analyzer output units (volts, millivolts, milliamps, etc.) against pollutant concentration should also be shown for analyzers not having an integral chart recorder. All such plots should consist of at

least seven (7) approximately equally spaced, identifiable points including 0 and 90 ± 5 percent of full scale. Calibration of analyzers for hydrocarbons corrected for methane should be based on either methane or methane equivalent. Methane may be used to calibrate "total hydrocarbon" or "methane" scales, but analyzers that read hydrocarbons corrected for methane directly should be calibrated with ethane, as methane equivalent. One ppm ethane is equivalent to 2 ppm methane.

(c) It is intended that analyzers be capable of unattended operation for at least three (3) days. Therefore, once the analyzer has been set-up and calibrated and the tests have started, manual adjustments or normal periodic maintenance on the analyzer is permitted only every three days. Automatic adjustments that the analyzer performs by itself are permitted at any time. Thus, the tests are to be carried out in a series of 3-day periods during which no manual adjustments are permitted. The strip chart records should clearly show when manual adjustments or periodic maintenance was made and describe the operations performed.

(d) If the analyzer should malfunction during any of the performance tests, the tests for that parameter should be re-initiated. A detailed explanation of the malfunction, remedial action taken, and whether recalibration was necessary (along with all pertinent records and charts) should be prepared. If more than one malfunction occurs, all performance test procedures for all parameters should be repeated.

(e) Normal analyzer operation or malfunction should not generate or present any hazards or hazardous conditions to operators or to the environment. Analyzers should include necessary safety devices to prevent such hazards and to prevent damage to the internal components

of the analyzer. Operation manuals should adequately warn of possible safety hazards and describe any necessary safety precautions.

(f) Tests for all performance parameters are to be completed on the same analyzer; use of multiple analyzers to accelerate testing is permitted only when testing alternate ranges of a multi-range analyzer.

3. GENERATION OF TEST ATMOSPHERES

(a) Table 2 gives preferred methods for generating test atmospheres as well as suggested methods of verifying the concentrations. Only one means of establishing the concentration of a test atmosphere is normally required. If the method of generation can produce accurate concentrations, verification is optional. If the method of generation is not accurate, then establishment of the concentration by some verification method is required.

(b) The test atmosphere delivery system should be designed and constructed so as not to significantly alter the test atmosphere composition or concentration during the period of the test. The delivery system should be fabricated from borosilicate glass or FEP Teflon.

(c) The output of the test atmosphere generation system must be sufficiently stable to obtain stable analyzer response during the required tests. If a permeation device is used for generation of a test atmosphere, the device, as well as the air passing over it, must be controlled to $\pm 0.1^{o}C$.

(d) All diluent air should be zero air free of contaminants likely to cause a detectable response on the analyzer.

(e) The concentration of each test atmosphere should be established or verified before or during each series of tests. Samples for verifying

Table 2. TEST ATMOSPHERES

Test gas	Generation	Verification
Ammonia	Permeation device. Similar to system described in References 1 and 2.	Indolphenol method, Reference 3.
Carbon monoxide	Cylinder of zero air or nitrogen containing CO as required to obtain the concentration specified in Table 3.	Use National Bureau of Standard (NBS)-certified standards whenever possible. If NBS standards are not available, obtain 2 standards, from independent sources, which agree within 2 percent, or obtain one standard and submit it to an independent laboratory for analysis, which must agree within 2 percent of the supplier's nominal analysis.
Ethane	Cylinder of zero air or nitrogen containing ethane as required to obtain the concentration specified in Table 3.	
Methane	Cylinder of zero air containing methane as required to obtain the concentration specified in Table 3.	
Nitric oxide	Cylinder[a] of "prepurified" nitrogen containing approximately 100 ppm NO. Dilute with zero air to concentration specified in Table 1.	Gas phase titration as described in Reference 4, Section 7.1.
Nitrogen dioxide	1. Gas phase titration as described in Reference 4.	1. Use an NO_2 analyzer calibrated with a gravimetrically calibrated permeation device.
	2. Permeation device, similar to system described in References 1 and 2.	2. Use an NO_2 analyzer calibrated by gas phase titration as described in Reference 4.
Ozone	Calibrated ozone generator as described in Reference 5, Appendix D.	Use an ozone analyzer calibrated by gas phase titration as described in Reference 4.
Sulfur dioxide	Permeation device. Similar to system described in reference method for SO_2, Reference 5, Appendix A.	P-rosaniline method. Reference 5, Appen-Appendix A.
Water	Pass zero air through distilled water at a fixed known temperature between 20° to 30°C such that the air stream becomes saturated. Dilute with zero air to concentration specified in Table 3.	Measure relative humidity by means of a dew point indicator, calibrated electrolytic or piezoelectric hygrometer or or wet/dry bulb thermometer.

Table 2 (continued). TEST ATMOSPHERES

Test gas	Generation	Verification
Zero air	1. Ambient air purified by appropriate scrubbers or other devices such that it is free of contaminants likely to cause a detectable response on the analyzer. 2. Cylinder of compressed zero air certified by the supplier or an independent laboratory to be free of contaminants likely to cause a detectable response on the analyzer.	

[a]Use stainless steel pressure regulator dedicated to the pollutant measured.

Ref. 1 - O'Keeffe, A.E., and G.C. Ortman. Primary Standards for Trace Gas Analysis. Anal. Chem. 38: 760, 1966.

Ref. 2 - Scaringelli, F.P., A.E. O'Keeffe, E. Rosenberg, and J.P. Bell. Preparation of Known Concentrations of Gases and Vapors With Permeation Devices Calibrated Gravimetrically. Anal. Chem. 42:871, 1970.

Ref. 3 - Tentative Method of Analysis for Ammonia in the Atmosphere (Indolphenol Method). Health Lab. Sciences. 10 (2): 115-118, April 1973.

Ref. 4 - Tentative Method for the Continuous Measurement of Nitrogen Dioxide (Chemiluminescent), Addenda C. Federal Register. 38(110): 28438, October 12, 1973.

Ref. 5 - National Primary and Secondary Ambient Air Quality Standards. Federal Register. 36(84):8186, April 30, 1971.

test concentrations should be collected from the test atmosphere delivery system as close as possible to the sample intake port of the analyzer under test.

(f) The accuracy of all flow measurements used to calculate test atmosphere concentrations should be documented and referenced to a primary standard. All flow measurements given in volume units should be standardized to 25°C and 760 mm Hg.

(g) Schematic drawings and other information showing complete procedural details of the test gas generation, verification, and delivery system should be included in the test results. All pertinent calculations should also be clearly indicated.

4. TEST PROCEDURES

(a) Range

(1) Technical Definition: Nominal minimum and maximum concentrations which the analyzer shall be capable of measuring. The nominal range is specified at the lower and upper range limits in concentration units, for example: 0-0.5 ppm.

(2) Test Procedure: This test is satisfied by a suitable calibration curve, as specified in Section 2 (b), showing analyzer response over the required range.

(b) Noise

(1) Technical Definition: Spontaneous, short duration deviations in the analyzer output, about the mean output, which are not caused by input concentration changes. Noise is determined as the standard deviation about the mean and expressed in concentration units.

(2) Test Procedure:

(i) Allow sufficient time for the analyzer to warm up and stabilize. Noise is determined at two concentrations using zero air and then a pollutant test gas concentration as indicated below. The noise specification in Table 1 applies to both of these tests.

(ii) Connect an integrating type digital meter (DM) suitable for the analyzer output and accurate to three significant digits, to measure the analyzer's output signal. Use of a chart recorder in addition to the DM is optional.

(iii) Measure zero air for 60 minutes. During this 60-minute interval, record twenty-five (25) DM readings at 2-minute intervals (Figure 1).

(iv) Convert each DM reading to concentration units by reference to the analyzer calibration curve as determined in Section 2 (b).. Label the converted DM readings r_1, r_2, r_3,....r_{25}.

(v) Calculate the standard deviation, S, as follows:

$$S = \sqrt{\frac{\sum_{i=1}^{25}(r_i)^2 - 1/25 \left(\sum_{i=1}^{25} r_i\right)^2}{24}} \text{ (ppm)}$$

where i indicates the i-th DM reading in parts per million.

(vi) Let S at 0 ppm be identified as S_0; compare S_0 to the noise specification given in Table 1.

Applicant _____ Date _____

Test No. _____

Analyzer _____ Range _____

READING NUMBER (i)	TIME	0% of URL		80% of URL	
		DM READING	r_i, ppm	DM READING	r_i, ppm
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					
$\sum_{i=1}^{25} r_i$					
$\sum_{i=1}^{25} r_i^2$					
S			S_0 =		S_{80} =

Figure 1. Form for noise data.

(vii) Repeat steps (iii) through (vi) using a pollutant test atmosphere concentration of 80 percent ± 5 percent of the upper range limit (URL) instead of zero gas, and let S at 80 percent of the URL be identified as S_{80}. Compare S_{80} to the noise specification given in Table 1.

(viii) Both S_0 and S_{80} must be less than or equal to the specification for noise to pass this test.

(c) Lower Detectable Limit

(1) Technical Definition: The minimum pollutant concentration that produces a signal of twice the noise level.

(2) Test Procedure:

(i) Allow sufficient time for the analyzer to warm up and stabilize. Measure zero air and record the stable reading as B_Z (Figure 2).

(ii) Generate and measure a pollutant test atmosphere concentration equal to the value for lower detectable limit specified in Table 1. The test atmosphere concentration may be generated or verified at a higher concentration, then accurately diluted with zero air to the final required concentration.

(iii) Record the analyzer's stable indicated reading in ppm, as B_L.

(iv) Determine the lower detectable limit (LDL) as $LDL = B_L - B_Z$. Compare this LDL value with the noise level, S_0, determined in Section 4 (b), for 0 concentration test atmosphere. LDL must be equal to or higher than

Applicant _____

Analyzer _____ Range _____

TEST PARAMETER		READING OR CALCULATION	TEST NUMBER														
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
LOWER DETECTABLE LIMIT		B_Z															
		B_L															
		$LDL = B_L - B_Z$															
INTERFERENCE EQUIVALENT	1	R_1															
		R_{11}															
		$IE_1 = R_{11} - R_1$															
	2	R_2															
		R_{12}															
		$IE_2 = R_{12} - R_2$															
	3	R_3															
		R_{13}															
		$IE_3 = R_{13} - R_3$															
	4	R_4															
		R_{14}															
		$IE_4 = R_{14} - R_4$															
	5	R_5															
		R_{15}															
		$IE_5 = R_{15} - R_5$															
	TOTAL	$IE_T = \sum_{i=1}^{\infty} \lvert IE_i \rvert$															

Figure 2. Form for data and calculations for lower detectable limit and interference equivalent.

2 times S_0 to pass this test.

(d) Interference Equivalent

(1) Technical Definition: Positive or negative response caused by a substance other than the one being measured.

(2) Test Procedure: The analyzer is to be tested for all substances likely to cause a detectable response. The analyzer is challenged, in turn, with each interfering agent specified in Table 3. In the event that there are substances likely to cause a significant interference that have not been specified in Table 3, these substances shall be tested at a concentration substantially higher than that normally found in the ambient air. The interference may be either positive or negative, depending on whether the analyzer's response is increased or decreased by the presence of the interferent. Interference equivalents are determined by mixing each interferent, one at a time, with the pollutant at the concentrations specified in Table 3, and comparing the analyzer's response to the response caused by the pollutant alone. Known gas-phase reactions that might occur between an interferent and the pollutant are designated by footnote c in Table 3. In these cases, the interference equivalent should be determined in the absence of the pollutant.

(i) Allow sufficient time for warm-up and stabilization of the analyzer.

(ii) For analyzers using a prefilter or scrubber based upon a chemical reaction to derive part of its specificity and requiring periodic service or maintenance, the analyzer shall be "conditioned" prior to each inter-

Table 3. INTERFERENT TEST CONCENTRATION

(parts per million)

Pollutant and analyzer type[b]	Interferents[a]						
	Ammonia	Sulfur Dioxide	Nitric Oxide	Ozone	Water Vapor	Carbon Monoxide	Methane
Nitrogen Dioxide, 0.1 ppm[d]							
Chemiluminescent	0.1[c]	0.5	0.5		20,000		
Spectrophotometric-wet chemical (azo-dye reaction)		0.5	0.5	0.5			
Electrochemical	0.1[c]	0.5	0.5	0.5	20,000[c]	50	
Spectrophotometric-gas phase	0.1[c]	0.5	0.5	0.5	20,000[c]	50	
NMHC[e], 2.0 ppm ethane[d]							
Flame ionization detector					20,000	50	4.0

[a]Concentrations of interferent listed must be prepared and controlled to ±10 percent of stated value.

[b]Analyzer types not listed should be challenged with appropriate concentrations of substances likely to cause an interference.

[c]Do not mix with pollutant.

[d]Concentration of pollutant used for test. These pollutant concentrations must be prepared to ±10 percent of stated value.

[e]Hydrocarbons corrected for methane.

ference test as follows:

(a) Service or perform the indicated maintenance on the scrubber or prefilter as directed in the analyzer's operating instructions.

(b) Before testing for each interferent, allow the analyzer to sample through the scrubber a test atmosphere containing the interferent at a concentration equal to the value specified in Table 3. Sampling shall be at the normal flowrate and shall be continued for six (6) continuous hours prior to testing.

(iii) Generate three (3) test atmosphere streams as follows:

(a) Test atmosphere P; Pollutant concentration.

(b) Test atmosphere I: Interferent concentration.

(c) Test atmosphere Z: Zero air.

(iv) Adjust the individual flow rates and the pollutant or interferent generators for the three test atmospheres as follows:

(a) The flowrates of test atmospheres I and Z shall be identical.

(b) The concentration of pollutant in test atmosphere P shall be adjusted such that when P is mixed (diluted) with either test atmosphere I or Z, the resulting concentration of pollutant shall be as specified in Table 3.

(c) The concentration of interferent in test atmosphere I shall be adjusted such that when I is mixed (diluted) with test atmosphere P, the resulting

concentration of interferent shall be equal to the value specified in Table 3.

(d) To minimize concentration errors caused by flow rate differences between I and Z, it is recommended that the flow rate of P be from 10 to 20 times larger than the flowrates of I and Z.

(v) Mix test atmosphere P and Z by passing the total flow of both atmospheres through a mixing flask.

(vi) Measure the mixture of test atmospheres P and Z. Allow for a stable reading, and record the reading, in concentration units, as R (Figure 2).

(vii) Mix test atmospheres P and I by passing the total flow of both atmospheres through a mixing flask.

(viii) Measure this mixture and allow for a stable reading. Record the reading, in concentration units, as R_I.

(ix) Calculate the interference equivalent as:

$$IE = R_I - R$$

IE must be equal to or less than the specification given in Table 1 for each interferent to pass the test.

(x) Follow steps (iii) through (ix), in turn, to determine the interference equivalent for each interferent.

(xi) For those interferents which cannot be mixed with the pollutant, as indicated by footnote c in Table 3, adjust the concentration of the interferent in test atmosphere I to the specified value without mixing with the pollutant test atmosphere. Determine IE as follows:

(a) Sample and measure test atmosphere Z (zero air).

Allow for a stable reading and record the reading, in concentration units, as R.

(b) Sample and measure the interferent test atmosphere I. If the analyzer is not capable of negative readings, be sure the analyzer (not the recorder) is adjusted to give an offset zero. Record the stable reading in concentration units as R_I, extrapolating the calibration curve, if necessary, to represent negative readings.

(c) Calculate IE = R_I - R. IE must be equal to or less than the specification in Table 1 to pass the test.

(xii) Sum the absolute value of all the individual interference equivalents. This sum must be equal to or less than the total interferent specification given in Table 1 to pass the test. (NOTE: Specifications for interferent equivalents are not intended to indicate the allowable measurement inaccuracy at the levels of the air quality standards. The interferent equivalent specifications are predicated on challenging the candidate analyzer with a maximal concentration of potential interferents.)

(e) Zero Drift, Span Drift, Lag Time, Rise Time, Fall Time, and Precision

(1) Technical Definitions:

(i) Zero Drift: The change in analyzer response to zero pollutant concentration, over 12- and 24-hour periods of continuous unadjusted operation.

(ii) Span Drift: The percentage change in analyzer response to an up-scale pollutant concentration over a 24-hour period of continuous unadjusted operation.

(iii) Lag Time: The time interval between a step change in input concentration at the analyzer inlet, and the first observable corresponding change in the analyzer response.

(iv) Rise Time: The time interval between initial response and 95 percent of final response after a step increase in input concentration.

(v) Fall Time: The time interval between initial response and 95 percent of final response after a step decrease in input concentration.

(vi) Precision: Variation about the mean of repeated measurements of the same pollutant concentration, expressed as one standard deviation about the mean.

(2) Tests for these performance parameters are to be accomplished over a period of seven (7) or more days. During this time, the line voltage supplied to the candidate analyzer and the ambient temperature surrounding the analyzer are varied from day to day. One test result for each performance parameter is obtained each test day for either seven (7) or fifteen (15) test days as necessary. If work schedules, slow analyzer response, or other factors prohibit completion of the entire test procedure in the available time each day, the tests may be divided and conducted separately in two 7- or 15-day test periods as necessary.

(3) During any test period, periodic maintenance and manual adjustments to the electronics or to the gas or reagent flows are permitted only once every three (3) days. Automatic adjustments that the analyzer performs by itself are permitted at any time. Any interruptions will require repeating the 3-day test period during which the interruption occurred.

(4) This test shall be conducted either in an uninterrupted period of seven (7) to fifteen (15) days, or in increments of three (3) consecutive days. For example, if the test is interrupted by weekends, it may be performed in 3-day increments where adjustments are made on Monday and readings are taken on Tuesday, Wednesday, and Thursday.

(5) The 24-hour test day may begin at any clock hour. The first 12 hours out of each test day are required for testing 12-hour zero drift. Tests for the other parameters are conducted during the remaining 12 hours.

(6) Table 4 gives the line voltage and room temperature to be used for each test day. The line voltage and temperature are to be changed to the specified values at the start of each test day (i.e., at the start of the 12-hour zero test). Initial adjustments (day zero) are made at a line voltage of 115 volts (rms) and a room temperature of 25^{o}C.

(7) Every three (3) days the analyzer may be adjusted and/or serviced according to the periodic maintenance procedures specified in the analyzer's operations manual. This must be done immediately after completion of the day's tests, at the voltage and temperature specified for that day, and only on test days

Table 4. LINE VOLTAGE AND ROOM TEMPERATURE TEST CONDITIONS

Test day	rms Line voltage[a]	Room temperature, °C[b]	Comment
0	115	25	Initial set-up and adjustments,
1	125	20	
2	105	20	
3	125	30	Adjustments and/or periodic maintenance permitted at end of tests.
4	105	30	
5	125	20	
6	105	20	Adjustments and/or periodic maintenance permitted at end of tests.
7	125	30	Examine test results to ascertain if further testing is required.
8	105	30	
9	125	20	Adjustments and/or periodic maintenance permitted at end of tests.
10	105	20	
11	125	30	
12	105	30	Adjustments and/or periodic maintenance permitted at end of tests.
13	125	20	
14	105	20	
15	125	30	

[a]Voltage specified shall be controlled to ±1 volt.

[b]Temperature specified shall be controlled to ±1°C.

3, 6, 9, and 12. If necessary, the beginning of the test days succeeding such service or adjustment may be delayed as necessary to complete the service or adjustment operation.

(8) All analyzer response readings to be recorded should first be converted to concentration units according to the calibration curve. Whenever a test atmosphere is to be measured, but a stable reading is not required, the test atmosphere need be measured only long enough to cause a change in analyzer response of at least 10 percent of full scale. Identify all readings and other pertinent data on the strip chart. Figure 3 illustrates the pattern of the required readings.

(9) Test Procedure

(i) Arrange to generate pollutant test atmospheres as follows:

Test Atmosphere	Pollutant Concentration
A_0	Zero gas
A_{20}	20 ± 5% of upper range limit
A_{30}	30 ± 5% of upper range limit
A_{80}	80 ± 5% of upper range limit
A_{90}	90 ± 5% of upper range limit

Test atmospheres A_0, A_{20} and A_{80} must be consistent during the tests and from day to day.

(ii) For steps (xxv) through (xxxi), a chart speed of at least 10 centimeters per hour should be used. The actual chart speed, chart speed changes, and time checks should be clearly marked on the chart.

(iii) Allow sufficient time for analyzer to warm up and stabilize at a line voltage of 115 volts and a room

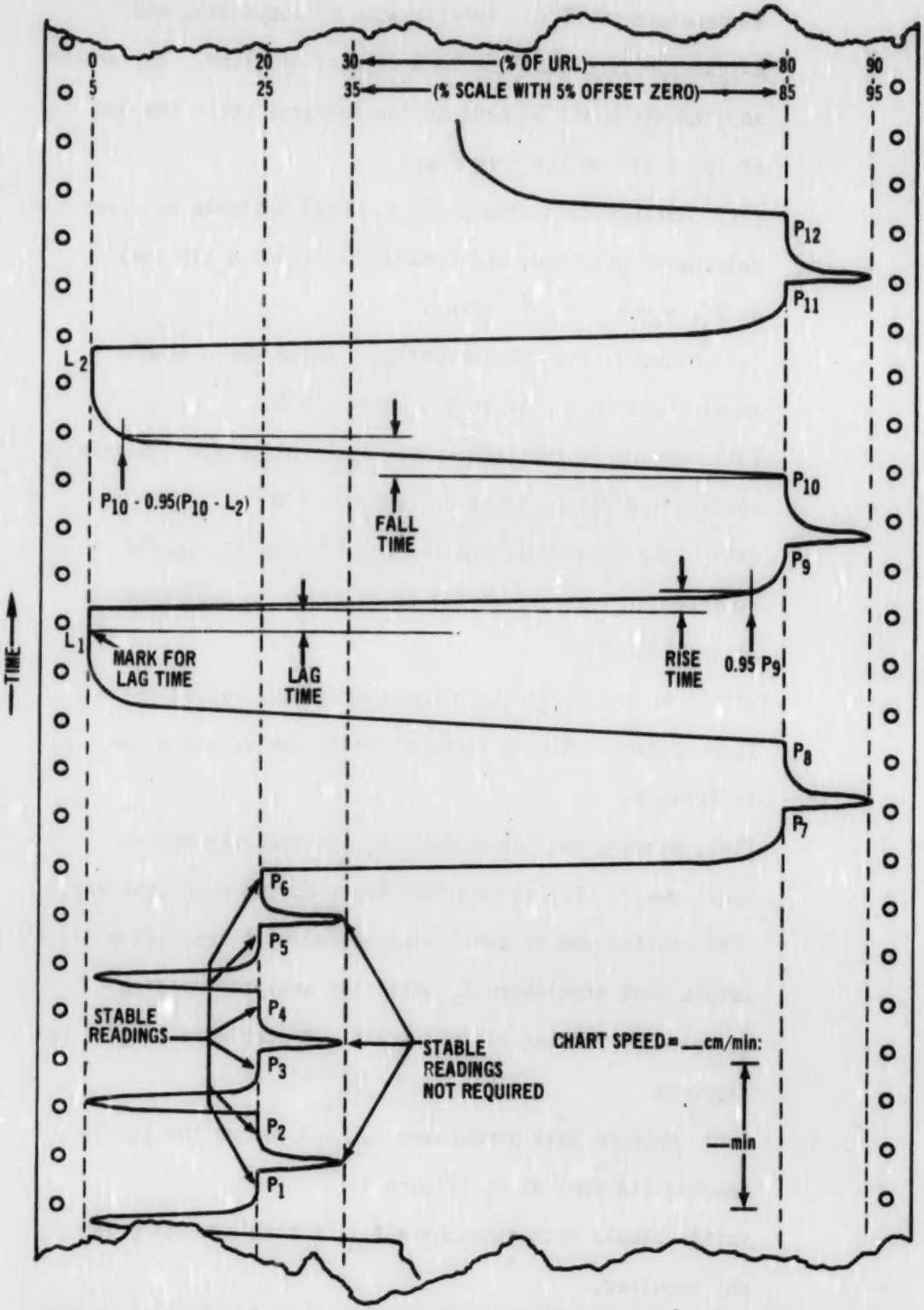

Figure 3. Example of a typical strip chart trace for the test procedure for drift, lag time, rise time, fall time, and precision.

temperature of 25°C. Recalibrate, if necessary, and adjust the zero baseline to 5 percent of chart. No further adjustments shall be made to the analyzer until the end of the tests on the third day.

(iv) Measure test atmosphere A_0 until a stable analyzer reading is obtained, and record this reading (in ppm) as Z'_η, where $\eta = 0$ (Figure 4).

(v) Measure test atmosphere A_{20}. Allow for a stable reading and record it as M'_η, where $\eta = 0$.

(vi) Measure a test atmosphere A_{80}. Allow for a stable reading and record it as S'_η, where $\eta = 0$.

(vii) The above readings for Z'_0, M'_0, and S'_0, should be taken at least seven (7) hours prior to beginning of test day 1.

(viii) At the beginning of each test day, adjust the line voltage and room temperature to the values given in Table 4.

(ix) Measure test atmosphere A_0 continuously for at least twelve (12) consecutive hours during each test day.

(x) At the end of the 12-hour zero drift test (step ix), sample test atmosphere A_0 until the analyzer reading is below 15 percent of full scale. A stable reading is not required.

(xi) Measure test atmosphere A_{20} and record the stable reading (in ppm) as P_1 (Figure 4).

(xii) Sample test atmosphere A_{30}; a stable reading is not required.

(xiii) Measure test atmosphere A_{20} and record the stable reading as P_2.

Applicant _____

Analyzer _____ Range _____

TEST DAY (n)	ANALYZER READING, ppm															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
DATE																
P_1																
P_2																
P_3																
P_4																
P_5																
P_6																
$\sum_{i=1}^{6} P_i^2$																
P_7																
P_8																
P_9																
P_{10}																
P_{11}																
P_{12}																
$\sum_{i=7}^{12} P_i^2$																
L_1																
L_2																
Z_n																
M_n																
S_n																
C_{max}																
C_{min}																

Figure 4. Form for recording data for drift and precision.

(xiv) Sample test atmosphere A_o; a stable reading is not required.

(xv) Measure test atmosphere A_{20} and record the stable reading as P_3.

(xvi) Sample test atmosphere A_{30}; a stable reading is not required.

(xvii) Measure test atmosphere A_{20} and record the stable reading as P_4.

(xviii) Sample test atmosphere A_o; a stable reading is not required.

(xix) Measure test atmosphere A_{20} and record the stable reading as P_5.

(xx) Sample test atmosphere A_{30}; a stable reading is not required.

(xxi) Measure test atmosphere A_{20} and record the stable reading as P_6.

(xxii) Measure test atmosphere A_{80} and record the stable reading as P_7.

(xxiii) Sample test atmosphere A_{90}; a stable reading is not required.

(xxiv) Measure test atmosphere A_{80} and record the stable reading as P_8. Increase chart speed to at least 10 centimeters per hour.

(xxv) Measure test atmosphere A_o. Record the stable reading as L_1.

(xxvi) Quickly switch the analyzer to measure test atmosphere A_{80} and mark the recorder chart to show the exact time when the switch occurred.

(xxvii) Measure test atmosphere A_{80} and record the stable reading as P_9.

(xxviii) Sample test atmosphere A_{90}; a stable reading is not required.

(xxix) Measure test atmosphere A_{80} and record the stable reading as P_{10}.

(xxx) Measure test atmosphere A_o and record the stable reading as L_2.

(xxxi) Measure test atmosphere A_{80} and record the stable reading as P_{11}.

(xxxii) Sample test atmosphere A_{90}; a stable reading is not required.

(xxxiii) Measure test atmosphere A_{80} and record the stable reading as P_{12}.

(xxxiv) Repeat steps (viii) to (xxxiii) each test day.

(xxxv) If zero and span adjustments are made after the readings are taken on test days 3, 6, 9, or 12, complete all adjustments; then measure test atmospheres A_o, A_{80}, and A_{20}. Allow for a stable reading on each and record the readings as Z'_n, S'_n, and M'_n, respectively, where n = the test day number.

(10) Determine the results of each day's tests as follows. Mark the recorder chart to show readings and determinations.

(i) Zero Drift:

(a) 12-hour. Examine the strip chart pertaining to the 12-hour continuous zero gas test. Determine the minimum (C_{min}) and maximum (C_{max}) readings (in ppm) during this period of 12 consecutive hours, extrapolating the calibration curve to negative concentration units if necessary. Determine the 12-hour zero drift (12ZD) as $12ZD = C_{max} - C_{min}$ (Figure 5).

(b) Calculate the 24-hour zero drift (24ZD) for the *n-th* test day as $24ZD_n = Z_n - Z_{n-1}$, or $24ZD_n = Z_n - Z'_{n-1}$ if zero adjustment was on the previous day, where $Z_n = \frac{L_1 + L_2}{2}$ for L_1 and L_2 taken on the *n-th* test day.

(c) Compare 12ZD and 24ZD to the zero drift specification in Table 1. Both 12ZD and 24ZD must be equal to or less than the specified value to pass the test for zero drift.

Applicant _____

Analyzer _____ Range _____

TEST PARAMETER		CALCULATION	n - th TEST DAY													
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Zero drift	12 hour	$12ZD = C_{max} - C_{min}$															
	24 hour	$Z = \frac{1}{4}(L_1 + L_2)$															
		$24ZD_n = Z_n - Z_{n-1}$															
		$24ZD_n = Z_n - Z'_{n-1}$															
Span drift	20% URL	$M_n = \frac{1}{6}\sum_{i=1}^{6} P_i$															
		$MSD_n = \frac{M_n - M_{n-1}}{M_{n-1}} \times 100\%$															
		$MSD_n = \frac{M_n - M'_{n-1}}{M'_{n-1}} \times 100\%$															
	80% URL	$S_n = \frac{1}{6}\sum_{i=7}^{12} P_i$															
		$USD_n = \frac{S_n - S_{n-1}}{S_{n-1}} \times 100\%$															
		$USD_n = \frac{S_n - S'_{n-1}}{S'_{n-1}} \times 100\%$															
Precision	20% URL	$P_{20} = \sqrt{\frac{1}{5}\left[\sum_{i=1}^{6} P_i^2 - \frac{1}{6}\left(\sum_{i=1}^{6} P_i\right)^2\right]}$															
	80% URL	$P_{80} = \sqrt{\frac{1}{5}\left[\sum_{i=7}^{12} P_i^2 - \frac{1}{6}\left(\sum_{i=7}^{12} P_i\right)^2\right]}$															

Figure 5. Form for calculating zero drift, span drift, and precision.

(ii) Span Drift

(a) Span drift at 20% of URL (MSD):

$$MSD_n = \frac{M_n - M_{n-1}}{M_{n-1}} \times 100\ \%, \text{ or}$$

$$MSD_n = \frac{M_n - M'_{n-1}}{M'_{n-1}} \times 100\ \%$$

if span adjustment was made on the previous day, where

$$\overline{M_n} = \frac{1}{6}\sum_{i=1}^{6} \overline{P_i},$$

n indicates the n-th test day, and i indicates the i-th reading on the n-th test day.

(b) Span drift at 80% of URL (USD):

$$USD_n = \frac{S_n - S_{n-1}}{S_{n-1}} \times 100\ \%, \text{ or}$$

$$USD_n = \frac{S_n - S'_{n-1}}{S'_{n-1}} \times 100\ \%$$

if span adjustment was made on the previous day, where

$$\overline{S_n} = \frac{1}{6}\sum_{i=7}^{12} \overline{P_i},$$

n indicates the n-th test day, and

i indicates the i-th reading on the n-th test day.

(c) Both USD and MSD must be equal to or less than the specification given in Table 1 to pass the test for span drift.

(iii) Lag Time: Determine, from the strip chart, the elapsed time in minutes between the mark made in step (xxvi) and the first observable (two times the noise level) analyzer response. This time must be equal to or less than the time specified in Table 1 to pass the test for lag time.

(iv) Rise Time: Calculate 95 percent of reading P_9 and determine, from the recorder chart, the elapsed time between the first observable (two times noise level) analyzer response and a response equal to 95 percent of the P_9 reading. This time must be equal to or less than the rise time specified in Table 1 to pass the test for rise time.

(v) Fall Time: Calculate 95 percent of $(P_{10} - L_2)$ and determine, from the strip chart, the elapsed time in minutes between the first observable decrease in analyzer response following reading P_{10} and a response equal to 95 percent of $(P_{10} - L_2)$. This time must be equal to or less than the fall time specification in Table 1 to pass the test for fall time.

(vi) Precision. Calculate precision for each day's test as follows:

(a) $$P_{20} = \sqrt{\frac{1}{5}\left[\sum_{i=1}^{6} P_i^2 - \frac{1}{6}\left(\sum_{i=1}^{6} P_i\right)^2\right]}$$

(b) $$P_{80} = \sqrt{\frac{1}{5}\left[\sum_{i=7}^{12} P_i^2 - \frac{1}{6}\left(\sum_{i=7}^{12} P_i\right)^2\right]}$$

(c) Both P_{20} and P_{80} must be equal to or less than the specification given in Table 1 to pass the test for precision.

Applicant _____ Analysts _____

Analyzer _____

_____

Range _____

PERFORMANCE PARAMETER		Table B-1 spec.	TEST 1	2	3	4	5	6	7	TEST 8	9	10	11	12	13	14	15	No. of test failures	Pass or fail
NOISE, ppm	0% URL (S_0)																		
	80% URL (S_{80})																		
LDL must be 2 x noise[a]																			
INTERFERENCE EQUIVALENT, ppm	IE_1																		
	IE_2																		
	IE_3																		
	IE_4																		
	IE_5																		
	TOTAL (IE_T)																		
ZERO DRIFT, ppm	12 hour (12ZD)																		
	24 hour (24ZD)																		
SPAN DRIFT, %	20% URL (MSD)																		
	80% URL (USD)																		
LAG TIME, min																			
RISE TIME, min																			
FALL TIME, min																			
PRECISION, ppm	20% URL (P_{20})																		
	80% URL (P_{80})																		

[a]Compare each test LDL reading with the corresponding noise measurements: LDL reading must exceed the 0% URL noise value by a factor of 2 to pass the test for LDL.

Figure 6. Form for summary of test results.

Table 5. SYMBOLS AND ABBREVIATIONS

B_L.....Analyzer reading at specified LDL concentration
B_Z.....Analyzer reading at 0 concentration for LDL test
DM.....Digital meter
C_{max}.....Maximum analyzer reading during 12ZD test
C_{min}.....Minimum analyzer reading during 12ZD test
i.....Subscript indicating the i-th quantity in a series
IE.....Interference equivalent
L_1.....First analyzer zero reading for 24ZD test
L_2.....Second analyzer zero reading for 24ZD test
M_n.....Average of $P_1 \ldots P_6$ for the n-th test day
M_n'.....Adjusted span reading at 20% of URL on the n-th test day
MSD.....Span drift at 20% of URL
n.....Subscript indicating the test day number
P.....Analyzer reading for precision test
P_i.....The i-th analyzer reading for precision test
P_{20}.....Precision at 20% of URL
P_{80}.....Precision at 80% of URL
R.....Analyzer reading of pollutant alone for IE test
R_I.....Analyzer reading with interferent added for IE test
r_i.....The i-th DM reading for noise test
S.....Standard deviation of noise readings
S_o.....Noise value (S) measured at 0 concentration
S_{80}.....Noise value (S) measured at 80% of URL
S_n.....Average of $P_7 \ldots P_{12}$ for the n-th test day
S_n'.....Adjusted span reading at 80% of URL on the n-th test day
URL.....Upper range limit
USD.....Span drift at 80% of URL
Z.....Average of L_1 and L_2
Z_n.....Average of L_1 and L_2 on the n-th test day
Z_n'.....Adjusted zero reading on the n-th test day
ZD.....Zero drift
12ZD.....12-hour zero drift
24ZD.....24-hour zero drift